SOLID SOLUTIONS OF NIOBIUM IN SYNTHETIC TITANITE

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Abstract

Synthetic (Ca1–xNa)x(Ti1–xNb)xOSiO4 and Ca(Ti1–x2Nb)xAlx)OSiO4 solid solutions have been prepared for x = 0.1 and 0.2 by ceramic methods and their crystal structure determined by Rietveld analysis. At ambient conditions, the isomorphic capacity of (FOH)-free titanite is ~0.25 apfu Nb in a single-site scheme of substitution (2VITi4+ ↔ VIAl3+ + VInb5+) and ~0.22 apfu Nb in a two-site scheme (VIICa2+ + VITi4+ ↔ VIna+ + VInb5+). All cations located at the VIX and VIY sites are disordered. Analysis of tetrahedron bond-lengths indicates the absence of Al3+ replacing Si4+ in coordination tetrahedra. All Nb-doped varieties of titanite adopt space group A2/a. Thus, both single-site and complex multivalent schemes of substitution destroy the coherence of the off-centering of chains of octahedra typical of the CaTiOSiO4 end member, resulting in a P21/a → A2/a phase transition. The (Ca1–xNa)x(Ti1–xNb)xOSiO4 scheme of substitution incorporates the larger cations at both the VIY and VIY sites, whereas the Ca(Ti1–x2Nb)xAlx)OSiO4 scheme involves only VIY-site (Al3+, Nb5+) cations, with a slightly smaller “average” radius. Unit-cell dimensions change insignificantly and vary sympathetically with the change of average radii of the cations in the (Ca1–xNa)x(Ti1–xNb)xOSiO4 series and vary insignificantly in the Ca(Ti1–x2Nb)xAlx)OSiO4 series. Both Nb-doped titanite and pure CaTiOSiO4 consist of distorted polyhedra. The seven-fold coordination polyhedra and octahedra in Nb-doped titanite are slightly less stretched as compared to those in pure CaTiOSiO4. The SiO4 tetrahedron is compressed in Nb-doped titanite as compared to CaTiOSiO4. The experimental data obtained suggest that the existence of a titanite analogue with more than 50 mol.% of NaNbOSiO4 end member is unlikely. The solid solution involving the smaller VI(Al,Nb) cations theoretically could be stabilized at high pressure, suggesting the existence of a potentially new species dominated by the Ca(AlNb)OSiO4 end member. The synthetic titanite compositions may be suitable for the sequestration of radioactive waste containing 94Nb.

Keywords: titanite, Rietveld analysis, crystal structure, distortion, niobium, aluminum, sodium, radwaste disposal.

Sommaire

Nous avons synthétisé les solutions solides (Ca1–xNa)x(Ti1–xNb)xOSiO4 et Ca(Ti1–x2Nb)xAlx)OSiO4 pour x égal à 0.1 et 0.2 par méthodes céramiques, et nous avons déterminé leur structure cristalline par la méthode Rietveld. A conditions ambiantes, la capacité de la titanite stoechiométrique à accepter le Nb est environ 0.25 apfu Nb dans un schéma impliquant un seul site (2VITi4+ ↔ VIAl3+ + VInb5+) et ~0.22 apfu Nb dans un schéma impliquant deux sites (VIICa2+ + VITi4+ ↔ VIna+ + VInb5+). Tous les cations situés sur les sites VIX et VIY sont désordonnés. Une analyse des longueurs des liaisons des tétraèdres montre que Al3+ ne remplace pas Si4+. Toutes les préparations de titanite contenant le Nb adoptent le groupe d’espace A2/a. Ainsi, les deux schémas de substitution, impliquant un seul site ou deux sites, détruisent la cohérence des déplacements dans les chaînes d’octaèdres de la titanite idéale CaTiOSiO4, provoquant ainsi une inversion de P21/a à A2/a. Dans le schéma de substitution (Ca1–xNa)x(Ti1–xNb)xOSiO4, les plus gros cations sont incorporés aux deux sites, VIX et VIY, tandis que dans le cas du schéma Ca(Ti1–x2Nb)xAlx)OSiO4, les cations (Al3+, Nb5+) sont uniquement sur le site VIY, qui possède un rayon moyen un peu plus petit. Les paramètres réticulaires varient de façon très mineure selon le changement en rayon ionique moyen des cations dans la série (Ca1–xNa)x(Ti1–xNb)xOSiO4 et encore moins dans la série Ca(Ti1–x2Nb)xAlx)OSiO4. La titanite dopée en Nb et la titanite pure CaTiOSiO4 contiennent des polyédres de coordiquence difformes. Les polyèdres à coordiquence sept et les octaèdres dans la titanite dopée au Nb sont légèrement moins étirés que ceux dans le CaTiOSiO4 pur. Le tétraèdre SiO4 est comprimé dans la titanite dopée au Nb en comparaison du tétraèdre dans le CaTiOSiO4 pur. Les données expérimentales obtenues semblent indiquer qu’un analogue de la titanite ayant plus de 50% (base molaire) du pôle NaNbOSiO4 n’est probablement pas stable. La solution solide impliquant les cations plus petits VI(Al,Nb) pourrait en théorie être stabilisée à pression élevée, ce qui laisse prévoir une nouvelle espèce ayant comme pôle Ca(AlNb)OSiO4. Les compositions synthétiques de titanite pourraient être appropriées pour la séquestration de déchets radioactifs contenant le 94Nb.

(Mots-clés: titanite, analyse Rietveld, structure cristalline, distorsion, niobium, aluminium, sodium, déchets radioactifs.)
INTRODUCTION

Niobium is a common minor constituent of natural titanite, \( ^{VII}X^{VI}YOSiO_4 \), where \( X = Ca, Na, REE, Y, Sr, Mn, \) and \( Y = Ti, Sn, Sb, Al, Fe, Zr, Ta, Nb \) (Sahama 1946, Černý & Riva di Sanseverino 1972, Paul et al. 1981, Sawka et al. 1984, Della Ventura et al. 1999, Tiepolo et al. 2002, Chakhmouradian & Zaitsev 2002, Chakhmouradian et al. 2003, Chakhmouradian 2004). Entry of Nb\(^{5+}\) into the titanite structure at the \( ^{VI}Y \) site is commonly balanced by (Al,Fe)\(^{3+}\) or by the replacement of Ca\(^{2+}\) by Na\(^{+}\) at the \( ^{VII}X \) site. Charge-balancing substitutions of \( O^{2-} \) by (F,OH)\(^{-}\) involving the anionic site \( O(1) \) also are possible. The most strongly niobian varieties of titanite are known to crystallize from the latest-forming low-temperature derivatives of alkaline rocks (Chakhmouradian 2004) and can contain up to 16.4 wt.% Nb\(_2\)O\(_5\) \([0.25 \text{ apfu Nb} \) (Liferovich & Mitchell 2005a)]).

Data on the crystal structure of naturally occurring Nb-rich titanite are limited to a single-crystal study of titanite from Mt. Somma, Italy containing 0.04 apfu Nb, and comparable amounts of Zr, OH and F. These data suggest that a single-site diadochy, \( 2Ti^{4+} \Rightarrow (Al,Fe)^{3+} + Nb^{5+} \), is primarily responsible for the incorporation of Nb at the \( ^{VI}Y \) site (Brigatti et al. 2004). A study of the structure of Nb-rich naturally occurring titanite is typically hindered by significant compositional inhomogeneity (Chakhmouradian 2004, Liferovich & Mitchell 2005a). For this reason, we have synthesized and refined the crystal structure of the compositional analogue of natural titanite containing 0.15 apfu Nb, which involves a two-site cationic scheme of substitution: \( ^{VII}Ca^{2+} + 2^{VII}Ti^{4+} \Rightarrow ^{VII}Na^{+} + ^{VII}Nb^{5+} + ^{VII}Zr^{4+} \) (Liferovich & Mitchell 2005a). Such a complex two-site substitution might permit the entry of more Nb into the structure than would be possible with a single-site substituted material.

In this contribution, we present experimental data regarding the synthesis of Nb-rich titanite together with observations on the response of the structure to single-site and two-site substitutions involving Nb.

THE CRYSTAL STRUCTURE AND PHASE TRANSITIONS OF TITANITE: AN OVERVIEW

The structure of titanite consists of kinked chains of corner-linked \( YO_6 \) octahedra sharing \( O(1) \) atoms (Fig. 1). The Si\(_6\) octahedra cross-link the chains of octahedra. Irregular \( XO_7 \) polyhedra form interlacing chains sharing edges via couples of oxygen atoms; these chains extend down [101]. The \( YO_6 \) and \( XO_7 \) chains are interconnected by shared edges. The titanite structure can be considered as a \([YO_6SiO_4]^{2-}\) framework.

![Fig. 1. Crystal structure of titanite. Lines represent the unit-cell boundaries. Arrows within TiO\(_6\) octahedra represent off-center displacement of six-coordinated atoms from the ideal position observed in the CaTiOSiO\(_4\), which disappears in the Na-Nb- and Nb-Al-doped synthetic titanite. The O(1), O(2) and O(3) atoms are shown as small black, light grey and grey spheres, respectively.](image-url)
with large cavities enclosing X atoms (essentially Ca) in irregular seven-fold cages (Speer & Gibbs 1976, Taylor & Brown 1976).

At ambient conditions, in CaTiO$_3$SiO$_4$, all V$^{IV}$Ti atoms occur in off-center positions that are displaced in the same direction within an individual TiO$_6$ chain, but in opposite directions between neighboring chains, resulting in $P2_1/n$ symmetry. According to Kunz & Brown (1994), this displacement of V$^{IV}$Ti atoms “out of their otherwise regular octahedron coordination” is caused by an electronic second-order Jahn–Teller effect occurring around the octahedrally coordinated cations of this d$^0$ transition metal. Kek et al. (1997) considered ordering of Ca in the V$^{IV}$X site as another trigger of the antiferroelectric displacement of V$^{IV}$Ti in the low-temperature CaTiO$_3$SiO$_4$.

The $P2_1/n$ to $A2/a$ phase transition in titanite can be induced by either an increase in pressure or temperature (Kunz et al. 1996, 2000, Kek et al. 1997, Angel et al. 1999), or occurs as a structural response to elemental substitutions involving the single YO$_6$ site, or complex substitutions at the YO$_6$ + O(1) or XO$_6$ + YO$_6$ sites (Higgins & Ribbe 1976, Speer & Gibbs 1976, Troitzsch & Ellis 2002).

Group-theoretical considerations for the CaTiO$_3$SiO$_4$ end-member allow stepwise changes in symmetry from $P2_1/a$ ($P2_1/n$ in conventional settings) to $A2/a$ (C$2/c$) via an intermediate disordered phase (Kek et al. 1997). The complete transformation results in centering of the octahedrally coordinated atoms in the YO$_6$ polyhedra due to equalization of the Y–O(1) and Y–O(1)' distances at P ≥ 3.5 GPa or T > 825 K (Kunz et al. 2000, Malcherek 2001, among others), and in oscillations of the V$^{IV}$X atom between two positions (Kek et al. 1997). An intermediate non-quenchable transition between 496 and 825 K (Ghose et al. 1991, Van Heurk et al. 1991, Salje et al. 1993) results from loss of long-range order and creation of antiphase boundaries between O(1)–Y–O(1)' dipoles, leaving domains of $P2_1/a$ symmetry on the unit-cell scale, but an overall, pseudocentered $A2/a$ symmetry on a long-range scale (Taylor & Brown 1976, Higgins & Ribbe 1976, Speer & Gibbs 1976, Kunz et al. 1996, Hughes et al. 1997, Troitzsch et al. 1999). The V$^{IV}$X atom is on a split position in this intermediate phase (Kek et al. 1997). Troitzsch & Ellis (2002) referred to the low-temperature phase with space group $P2_1/a$ as α, the intermediate $A2/a$ phase as β, and the high-P, high-T phase with true $A2/a$ symmetry as γ titanite. A further temperature-driven phase transition is possible above 1150 K (Chrosch et al. 1997). Conventionally, the α → β modification is referred to as “the $P2_1/a$ to $A2/a$ phase transition”, bearing in mind that it probably does not strictly represent the entire $P2_1/a$ → $A2/a$ transformation (Troitzsch & Ellis 2002).

In pure CaTiO$_3$SiO$_4$, different types of polyhedra have different responses to distortions induced by both high pressure and high temperature. The SiO$_4$ tetrahedra show a strong angular distortion with only minor change in bond lengths, whereas the polymerized CaO$_7$ polyhedra are significantly distorted, and TiO$_6$ octahedra rotate rigidly (Kunz et al. 2000).

Compositional changes drive phase-transitions in titanite are similar to those driven by high pressure or high temperature (Troitzsch & Ellis 2002, and references therein). Doping of the YO$_6$ site with the smaller Al$^{3+}$ ions, balanced by (F,OH)– at the O(1) site, results in the α → β transition at low Al + (F,OH) contents and a further “β → γ′”-like modification in more Al-rich titanite (Troitzsch & Ellis 2002). Stabilization of β titanite is possible at ambient conditions by means of two-site substitutions involving as little as 5 mol.% V$^{IV}$Al$^{3+}$ coupled with 5 mol.% charge-balancing V$^{IV}$D$_2$O$^{3+}$ (Hughes et al. 1997), whereas in the case of substitutions involving octahedrally coordinated cations balanced by an equal amount of F– at the O(1) site, the β dimorph becomes stable in the range of 9–18.2 mol.% V$^{IV}$Al$^{3+}$ (Troitzsch et al. 1999). This difference is due to relief of the underbonding of the bridging O(1) anions at antiphase boundaries, created in response to long-range disorder, and stabilization of the β form of titanite is more easily induced by substitutions at the seven-fold site (Hughes et al. 1997).

Here, we provide data on the response of the (OH,F)-free titanite structure to the entry of Nb with concomitant multivalent substitutions at the octahedral site or in the seven-fold site. These schemes of substitution have been investigated for the synthetic series (Ca$_1$–xNa$_x$)(Ti$_{1–}$xNb$_x$)O$_2$SiO$_4$ and Ca(Ti$_{1–}$_xNb$_x$Al$_x$)O$_2$SiO$_4$ (x = 0.1 and 0.2). Studies of other schemes of substitution involving Nb, as well as Ta, are in progress.

**Experimental and Analytical Techniques**

For consistency, we tried to prepare all samples by the same solid-state ceramic techniques from stoichiometric amounts of CaO$_3$SiO$_4$ (wollastonite polymorph 1A), TiO$_2$, Nb$_2$O$_5$, Al$_2$O$_3$, and Na$_2$CO$_3$. The reagents, dried at 120°C for several days, were mixed, ground in an agate mortar under acetone, and calcined in air for 24 h at 1000°C. After regrinding for 1 h, the samples were pelleted at a pressure of 10 tonnes per cm$^2$, and then heated in air for 96 h at 1175°C with further grinding (and pellet preparation) after the first 48 h and quenching in air. The crystal-structure parameters of the synthetic CaTiO$_3$SiO$_4$ obtained by this method of synthesis are close to those obtained from synchrotron data given by Kek et al. (1997) for CaTiO$_3$SiO$_4$ (Liferovich & Mitchell 2005b). Homogeneous samples of Al–Nb-doped titanite were prepared in this manner. Homogeneous Na–Nb-doped titanite was not formed during 96 hours of solid-state reaction. Longer-duration sintering resulted in volatilization of Na. The successful synthesis of the Na–Nb-doped titanite was performed by melting the samples at 1225°C for ½ hour. The samples subjected to melting contained 5% excess of Na after pre-sintering as described above. The melted
samples were cooled to 1175°C, and then sintered for 24 hours followed by quenching. Homogeneous products were obtained for Ca0.9Nb0.1Ti0.9Nb0.1O3 and Ca0.8Nb0.2Ti0.8Nb0.2O3SiO4.

The synthetic materials were investigated by energy-dispersion X-ray spectrometry (EDXA) using a JEOL JSM–5900 scanning electron microscope equipped with a LINK ISIS 300 analytical system. Raw EDS spectra were acquired for 130 s (five times) with an accelerating voltage of 20 kV, and beam current of 0.475 nA. The spectra were processed with the LINK ISIS–SEMQUANT quantitative software package, with full ZAF corrections applied. The following well-characterized minerals and synthetic compounds were used as analytical standards: ilmenite (Ti), corundum (Al), wollastonite (Ca), pyroxene glass DJ35 (Si), loparite (Nb), and jadeite (Na). The accuracy of Na analysis was cross-checked by the control compositions of natural natrolite and analcime.

Powder X-ray-diffraction (XRD) patterns were obtained at room temperature using a Philips 3710 diffractometer (T = 20°C; CuKα radiation; 2θ range 9°–145°, Δ2θ step 0.02° per 4 s). The patterns were analyzed by the Rietveld method using the Bruker AXS software TOPAS 2.1 (Kern & Coelho 1998). In addition, high-resolution XRD patterns were obtained in the 2θ range 31.7°–33.4° (Δ2θ step 0.005°; counting time per step: 30 s).

The ATOMS 6.0 software (Dowty 1999) was used to determine framework angles and interaxial angles for calculation of indices of bond-angle variation. The IVTON program (Balic-Žunić & Vicković 1996) was employed to obtain selected bond-lengths and to characterize the coordination spheres of the cations.

**RESULTS AND DISCUSSION**

The samples of sodic niobian and aluminian niobian titanite synthesized here consist of fine-grained aggregates with average grain-size of 10–15 μm, containing very little amount of by-products (1.5–3.4 wt.% in total). Some of the SiO2 impurity is considered to have been introduced by use of an agate mortar during sample preparation.

Synthesis of the entire (Ca1/2–1/2Nb)x(Ti1/2–1/2Nb)y)O3SiO4 and Ca(Ti1–x2/3Nb)x/3Al)O3SiO4 series was attempted, but was successful only for the compositional range of x = 0.1 and 0.2. No significant compositional heterogeneity was revealed by back-scattered electron (BSE) imagery for the compounds with x = 0.1 and 0.2 in both series.

For experiments with x > 0.2, SEM BSE images and XRD patterns reveal conspicuous compositional heterogeneity and demonstrate the presence of wollastonite (transformed to the 4A polymorph), rutile, complex titanates, and niobates. In addition, the amount of starting material remaining as non-reacted phases increases with x. The titanium-free end-member compounds with x = 1 did not form any titanite-structured phases. SEM EDXA data for run products obtained for 0 ≤ x ≤ 0.2 agree well with results for refinements of VIIx and VIY site-occupancies for the same samples using the Rietveld technique. The most niobian composition of the titanite obtained for runs with x > 0.3 in the Ca(Ti1–x2/3Nb)x/3Al)O3SiO4 series is (wt.% [apfu cation]): 5.6 [0.22] Al2O3, 27.6 [0.93] SiO2, 27.6 [0.99] CaO, 23.5 [0.6] TiO2, and 16.5 [0.25] Nb2O5, total 100.8 [3.0]. These data indicate that x = 0.25 apfu Nb is the empirical limit for diadochy between Nb and Ti in the octahedral site of the (F,OH)-free structure at ambient conditions. Crystal structures of titanite samples produced in runs with x > 0.2 are not considered here because the results of our refinements are not robust owing to the presence of significant amounts of impurities.

**Rietveld refinement**

For the Nb-doped varieties of titanite synthesized, powder X-ray diffractometry does not demonstrate the presence of 221 and 212 reflections, which occur clearly in the high-resolution XRD pattern of the pure CaTiO3SiO4 end member (Fig. 2). Given that extinction rules do not allow the k + l = odd reflections in the space group A2/a (Taylor & Brown 1976, Hollabaugh & Foit 1984, Kunz et al. 1996), we conclude that doping of titanite with Nb at ambient pressure according to either the single- or two-site scheme of substitution results in the stabilization of an A2/a dimorph in accordance with constraints maintained for titanite structure by group-theoretical considerations (Kek et al. 1997).

For Rietveld refinement of the A2/a-structured Nb-bearing varieties of titanite, we used as starting parameters the atom coordinates given by Mongiorgi & Riva di Sanseverino (1968). Figure 2 is a portion of the Rietveld refinement plot for the synthetic CaTi1.6Al0.4Nb0.2O3SiO4 titanite (“AlNb2”) over the 2θ range from 15 to 100° (note that the actual refinement is over the 9–145° 2θ range).

Agreement factors and crystal-structure parameters for Nb-bearing sodic and aluminian titanite are listed in Table 1 in comparison with crystal-structure parameters calculated for CaTiO3SiO4 on the basis of synchrotron radiation data published by Kek et al. (1997). Positional parameters and thermal parameters of the atoms obtained for Nb-bearing titanite are listed in Table 2. Selected bond-lengths are given in Table 3. All cations located at the VIIx and VIY sites are disordered. Refinement of the site occupancies shows no vacancies at cationic sites within the accuracy of the Rietveld results.
Geometry of sites in Nb-rich aluminous and sodic titanite

The \((\text{Ca}_{1-x}\text{Na}_x)(\text{Ti}_{1-x}\text{Nb}_x)\text{OSiO}_4\) scheme of substitution incorporates slightly larger cations at both the \(\text{VII}^X\) and \(\text{VI}^Y\) sites, whereas the \(\text{Ca}(\text{Ti}_{1-2x}\text{Nb}_x\text{Al}_x)\text{OSiO}_4\) scheme involves only \((\text{Al}^{3+},\text{Nb}^{5+})\) cations with a slightly smaller “average” radius (Shannon 1976) at the \(\text{VI}^Y\) site. Unit-cell dimensions change insignificantly in varieties of Nb-rich titanite and vary sympathetically with average radii of cations at the \(\text{VII}^X\) and \(\text{VI}^Y\) sites in the \((\text{Ca}_{1-x}\text{Na}_x)(\text{Ti}_{1-x}\text{Nb}_x)\text{OSiO}_4\) series. In the case of the \(\text{Ca}(\text{Ti}_{1-2x}\text{Nb}_x\text{Al}_x)\text{OSiO}_4\) series, these variations are negligible (Table 1).

The mean cation–oxygen distances within the \(\text{X}^\text{O}_7\) and \(\text{Y}^\text{O}_6\) coordination polyhedra vary insignificantly (Table 1). The \(<\text{X}–\text{O}>\) distances are statistically very similar for all the varieties of titanite obtained here and pure \(\text{CaTiOSiO}_4\) described by Kek et al. (1997) and Liferovich & Mitchell (2005b). Entry of \(\text{Nb}^{5+}\) at the \(\text{VI}^Y\) site, being slightly larger than \(\text{Ti}^{4+}\) \([\text{VIR} = 0.64 \text{ and } 0.605 \text{ Å, respectively (Shannon 1976)}]\), does not affect the \(<\text{Y}–\text{O}>\) distances in the Na–Nb-doped titanite. The \(<\text{Y}–\text{O}>\) distances decrease in the Nb–Al-doped titanite owing to entry at the \(\text{VI}^Y\) site of \((\text{Al}_{0.5}\text{Nb}_{0.5})\), with an average cationic radius slightly smaller than that of \(\text{Ti}^{4+}\) \([\text{VIR} = 0.59 \text{ Å}]\).

The volume of the \(\text{SiO}_4\) tetrahedron and the mean \(<\text{Si}–\text{O}>\) bond-length in the Nb-bearing varieties of titanite are less than those in the \(\text{CaTiOSiO}_4\) end member (Table 1). The dimensions of the \(\text{SiO}_4\) tetrahedron decrease stepwise with the double-site substitution \(\text{VI}^\text{Na}^+ + \text{VI}^\text{Nb}^{5+} \leftrightarrow \text{VI}^\text{Ca}^{2+} + \text{VI}^\text{Ti}^{4+}\) (Table 1), and do not change with \(x\) in the case of single-site substitution \(\text{VI}^\text{Al}^{3+} + \text{VI}^\text{Nb}^{5+} \leftrightarrow \text{VI}^\text{Ti}^{4+}\). Observed deviations of the mean bond-lengths from those in the Al-free \(\text{SiO}_4\) tetrahedron are conventionally used for considering possible substitutions of the larger \(\text{Al}^{3+}\) for the smaller \(\text{Si}^{4+}\) \([\text{IVR} = 0.39 \text{, IVRS} = 0.26 \text{ Å (Shannon 1976)}]\) at the tetrahedral site(s) of various silicates and aluminosilicates. A quantitative model has not yet been developed for infinite framework-type structure(s) containing tetrahedra and octahedra such as titanite, although some semiquantitative comparisons with well-studied tectosilicates seem possible. Thus, the \(<\text{Si}–\text{O}>\) distances in completely ordered anorthite range from 1.608 to 1.617 Å, whereas the \(<\text{Al}–\text{O}>\) distances range from 1.742 to 1.755 Å (Wainwright & Starkey 1971, Ghose et al. 1993). Similar mean \(<\text{Si}–\text{O}>\) distances are found in the following ordered aluminosilicates: lisenite: 1.619 Å, 1.620 Å, 1.622 Å and 1.623 Å (Rossi et al. 1986), slawsonite: 1.624 Å (Griffen et al. 1977), paracelsian: 1.613 Å (Chiari et al. 1985), nepheline: 1.603–1.616 Å (Tait et al. 2003), stromalite: 1.609 and 1.619 Å (Liferovich et al. 2006), and banalsite: 1.621 and 1.622 Å (Liferovich et al. 2006). Hence, the similarity of the \(<\text{T}–\text{O}>\) distances for the \(\text{AlNb}_1\) and \(\text{AlNb}_2\) samples \([1.618(9) \text{ and } 1.621(10) \text{ Å, respectively (Table 1)}]\) to \(<\text{Si}–\text{O}>\) bond lengths in completely ordered tectosilicates implies the absence of \(\text{Si} \leftrightarrow \text{Al}\) substitution at the tetrahedral site in the niobian–aluminian varieties of titanite.

Fig. 2. Rietveld refinement plot of the X-ray powder-diffraction data for synthetic titanite \(\text{CaTi}_{0.6}\text{Nb}_{0.2}\text{Al}_{0.2}\text{OSiO}_4\) at room temperature. For details of the refinement, see text and Table 2.
The volume of the $XO_7$ coordination polyhedron in the \(\text{Ca}(\text{Ti}_{1-x}\text{Nb}_x\text{Al}_x)\text{OSiO}_4\) series (Table 1) is similar to that in the \(\text{CaTiOSiO}_4\) end member described by Kek et al. (1997) and Liferovich & Mitchell (2005b). The volume of the $XO_7$ coordination polyhedron in the \((\text{Ca}_{1-x}\text{Na}_x)(\text{Ti}_{1-x}\text{Nb}_x)\text{OSiO}_4\) is larger owing to entry of the larger $\text{Na}^+$ cation (Table 1).

The distortion index introduced by Shannon (1976) is useful to illustrate polyhedron bond-length distortion, i.e., \(\Delta_d = l / n[\Sigma (r_i - \bar{r})^2 / n]^{1/2}\), where \(r_i\) and \(\bar{r}\) are individual and average bond-lengths, respectively (Shannon 1976).

The bond-angle variance index reflects twisting and tilting deformation of coordination polyhedra.
The crystalstructure response to the substitution of $^{4+}$Ti$^+$ for $^{4+}$Ti$^+$ in titanite has been studied in the 
(Ca$_{1-x}$Na$_x$)(Ti$_{1-x}$Nb$_x$)O$_3$SiO$_4$ solid-solution series synthesized by ceramic methods at
ambient pressure, with quenching in air. Our findings demonstrate that (OH,F)-free titanite varieties doped with Nb via both a single-site and a complex two-site schemes of substitution at $x \geq 0.05$ and 0.2 adopt the
$A2/a$ space group and are stable at ambient pressure and temperature. Both the single-site and two-site schemes of substitution affect the coherency of the off-centering of the $^4$Y atom in the chains of octahedra and result in an antiferroelectric-to-paraelectric transition (Speer & Gibbs 1976, Ghose et al. 1991, Van Heurk et al. 1991, Kek et al. 1997). In part, our study confirms the previously published data for a phase transition driven by replacement of $\leq 0.05$ apfu $^{4+}$Ca$^{4+}$ and 0.05 apfu $^{4+}$Ti$^{4+}$
(Hughes et al. 1997) or in the range of 0.09–0.18 apfu $^{4+}$Ti$^{4+}$ and O(1)$^\circ$ by $^{4+}$(Al,Fe)$^{4+}$ and (OH,F)$^-$ (Troitzsch et al. 1999). Nevertheless, any conclusions on the nature of the centering of the $^4$Y atom in Nb-rich titanite, and thus discrimination between the $A2/a$-structured $\beta$ and $\gamma$ phases introduced by Troitzsch & Ellis (2002), are not possible on the basis of the routine X-ray powder-diffraction technique.

The extent of stretching of the seven-fold coordination polyhedra and octahedra decreases with entry of Nb into CaTiOSiO$_4$. Deformations of octahedra induced by tilting and twisting are 4–5 times less in the Nb-doped titanite varieties than in pure CaTiOSiO$_4$. The SiO$_4$ tetrahedron is compressed and more tilted and twisted in the Nb-doped titanite varieties than in pure CaTiOSiO$_4$.

The empirical limit for entry of Nb to the ($^4$OH)$^-$-free titanite structure at ambient pressure is -0.25 apfu Nb in Nb–Al titanite (ca. 16.5 wt.% Nb$_2$O$_5$) and -0.22 apfu Nb in Na–Nb titanite. The limit may probably be greater in natural varieties of titanite, where contiguous substitutions involving for example, OH$^- + F^-$ at the (O1) site or vacancies at cation sites, can occur.

The experimental data suggest that the existence of a titanite analogue with more than 50 mol.% of the NaNbOSiO$_4$ end member is unlikely. The solid solution...
involving the smaller $^{\text{VI}}(\text{Al}_{0.5}\text{Nb}_{0.5})$ cations theoretically might be stabilized at high pressure, suggesting the existence of a potentially new species with dominance of the Ca(Al$_{0.5}$Nb$_{0.5}$)OSiO$_4$ end member, as has been proposed by Černý et al. (1995) for analogs of titanite enriched in (Nb,Ta).

The tolerance of the titanite structure to entry of Nb implies that the compositions of synthetic titanite might be suitable for the sequestration of radioactive waste containing $^{94}$Nb and other isotopes of Nb.

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**References**


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